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<p>(21) International Application Number: PCT/SE99/01113</p> <p>(22) International Filing Date: 18 June 1999 (18.06.99)</p> <p>(30) Priority Data:</p> <table border="0"> <tr> <td>60/090,507</td> <td>24 June 1998 (24.06.98)</td> <td>US</td> </tr> <tr> <td>98850112.8</td> <td>24 June 1998 (24.06.98)</td> <td>EP</td> </tr> </table> <p>(71) Applicant (for all designated States except US): AKZO NOBEL N.V. [NL/NL]; P.O. Box 9300, NL-6800 SB Arnhem (NL).</p> <p>(71) Applicant (for SE only): EKA CHEMICALS AB [SE/SE]; S-445 80 Bohus (SE).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (for US only): BIERMANN, Christian [DE/DE]; Konenstrasse 12, D-52349 Düren (DE). MACHEREY, Heribert [DE/DE]; Altenweiher 15, D-52372 Kreuzau (DE). GORZYNSKI, Marek [DE/DE]; Am Courtenbachshof 3, D-52349 Düren (DE).</p> <p>(74) Agent: NYANDER, Johan; Eka Chemicals AB, Patent Dept., P.O. Box 11556, S-100 61 Stockholm (SE).</p>	60/090,507	24 June 1998 (24.06.98)	US	98850112.8	24 June 1998 (24.06.98)	EP	<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p><b>Published</b></p> <p><i>With international search report.</i></p> <p><i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
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(54) Title: IONIC POLYURETHANES

(57) Abstract

The invention relates to a process for the production of charged polyurethanes comprising reacting isocyanate groups of a polyisocyanate with hydroxyl groups of alcohols comprising (i) a first alcohol selected from one or more diols containing at least 10 carbons atoms; (ii) a second alcohol selected from alkylene diols having not more than 8 carbon atoms, alkyleneoxy diols having not more than 8 carbon atoms, polyols, and mixtures thereof; (iii) a third alcohol selected from (a) diols containing a charged group or atom, (b) diols containing an uncharged group or atom capable of charge formation and at least partially converting the uncharged group or atom into a charged group or atom, (c) polyols and further reaction of one or more hydroxyl group derived from the polyol with a compound containing a charged group or atom or a compound containing an uncharged group or atom capable of charge formation and at least partially converting said uncharged group or atom into a charged group or atom, and mixtures thereof. The invention further relates to charged polyurethane obtainable by the process, an aqueous dispersion thereof and the use thereof in a method of surface-treating a material in sheet or web form by applying the charged polyurethane to the surface of the material.

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## IONIC POLYURETHANES

Field of the Invention

This invention relates to charged polyurethanes, aqueous dispersions of  
5 charged polyurethanes, a process for their preparation and their use as additives in the  
manufacture of paper.

Background of the Invention

It is known in the art to use charged polyurethanes as external and internal sizing  
agents in the manufacture of paper. For instance, U.S. Pat. No. 3,971,764 discloses sizing  
10 agents based on cationic polyurethanes prepared by (i) reacting an aliphatic diol having an  
aliphatic substituent with at least 10 carbon atoms with a polyisocyanate to form a pre-  
polymer with terminal isocyanate groups which is subsequently reacted with (ii) a diol  
containing a tertiary nitrogen atom which is subsequently converted into the corresponding  
ammonium compound, or (iii) a diol containing a nitrogen atom previously converted into  
15 the corresponding ammonium compound. Similarly, U.S. Pat. No. 4,096,127 discloses  
sizing agents based on anionic polyurethanes prepared by step (i) above followed by  
reacting the obtained prepolymer with (iv) an aliphatic diol containing an acid group  
capable of salt formation and at least partially converting the acid group into a salt by  
reaction with a base, or (v) an aliphatic diol which carries a salt group. U.S. Pat. No.  
20 4,777,224, also discloses sizing agents based on anionic polyurethanes prepared by  
steps (i), (iv) and (v) above and with the additional use of a polyether compound with at  
least one OH group. Polyurethanes of these types generally result in good sizing response  
using low dosages of sizing agent. However, there is still a need for sizing agents based on  
charged polyurethanes with improved sizing, stability and application properties.

25 It is accordingly an object of this invention to provide charged polyurethanes and  
aqueous dispersions thereof with improved sizing, stability and application properties.  
Further objects will appear hereinafter. The objects of the invention are achieved by a  
process for the production of charged polyurethanes, charged polyurethanes obtainable  
by the process, aqueous dispersions of charged polyurethanes and the use thereof, as  
30 further defined in the claims.

Summary of the Invention

The present invention relates to a process for the production of charged  
polyurethanes which comprises reacting a polyisocyanate with alcohols comprising (i) a first  
alcohol selected from one or more diols containing at least 10 carbon atoms; (ii) a second  
35 alcohol selected from alkylene diols and alkyleneoxy diols containing not more than 8  
carbon atoms, polyols, and mixtures thereof; (iii) a third alcohol selected from (a) diols

containing a charged group or atom, (b) diols containing an uncharged group or atom capable of charge formation and at least partially converting the uncharged group or atom into a charged group or atom, (c) polyols and further reaction with a compound containing a charged group or atom or a compound containing an uncharged group or atom capable of charge formation and at least partially converting the uncharged group or atom into a charged group or atom, and mixtures thereof.

#### Detailed Description of the Invention

The present invention generally relates to a process for the production of charged polyurethanes and charged polyurethanes obtainable by the process. The process comprises reacting isocyanate groups of a polyisocyanate with hydroxyl groups of di- and/or polyhydric alcohols comprising (i) a first alcohol selected from one or more diols containing at least 10 carbon atoms; (ii) a second alcohol selected from alkylene diols containing not more than 8 carbon atoms, alkyleneoxy diols containing not more than 8 carbon atoms, polyols, and mixtures thereof; (iii) a third alcohol selected from (a) diols containing a charged group or atom, (b) diols containing an uncharged group or atom capable of charge formation and at least partially converting the uncharged group or atom into a charged group or atom, (c) polyols and further reaction of one or more hydroxyl groups of the polyol with a compound containing a charged group or atom or a compound containing an uncharged group or atom capable of charge formation and at least partially converting the uncharged group or atom into a charged group or atom, and mixtures thereof.

Charged polyurethanes encompassed by this invention comprises polyurethanes containing anionic and/or cationic groups, thereby forming anionic, amphoteric and cationic polyurethanes. According to the present invention there is provided anionic, amphoteric and cationic polyurethanes with outstanding properties. Aqueous dispersions of the present charged polyurethanes provide improved sizing which means that lower levels of sizing agent can be used to give a corresponding sizing effect, thereby leading to cost reduction and economic benefits. Further characteristics observed with the dispersions of charged polyurethanes of this invention include less foaming, very good or improved stability, compatibility, glueability, sizing response and coating performance over a broad pH range and when used in surface sizing, precoating and coating applications in combination with conventionally used components, e.g. electrolytes, starch and derivatives thereof, pigments, other synthetic polymers, etc., as well as improved toner adhesion and ink jet properties.

The process of this invention can be carried out in several ways. It is possible to react the polyisocyanate with the first, second and third alcohols simultaneously, i.e. in a

so-called one-shot process. For instance, this mode of operation can be employed when using as the third alcohol (b) a diol containing an uncharged group or atom capable of charge formation, where charge formation suitably takes place when the polyurethane has been formed. However, it is generally preferred to carry out the process as a two-step or three-step process, for example by introducing the alcohols one after another into the process for reaction. The terms "one-shot process", "two-step process" and "three-step process", as used herein, refers to processes where the alcohols are introduced into the reaction medium for reaction essentially simultaneously, in two steps and in three steps, respectively. Running the process in at least two steps makes it possible to react the polyisocyanate with the alcohol(s) initially introduced into the reaction medium so as to form a preliminary adduct or prepolymer with isocyanate group(s), usually in a terminal position, and chain-lengthening the preliminary adduct by reaction with the alcohol(s) subsequently introduced into the reaction medium, the latter alcohol(s) functioning as a chain-extender, or chain-lengthening agent, or branching agent. Preferably the first and second alcohols are introduced into the process for reaction before introducing the third alcohol into the process. The first alcohol can be introduced into the process before, simultaneously with or after the second alcohol. In a preferred embodiment of the invention, the polyurethane is prepared by reacting the polyisocyanate with the first alcohol to form a preliminary adduct having terminal isocyanate groups; chain-lengthening the preliminary adduct by reaction with the third alcohol, and optionally conversion of any uncharged groups or atoms as defined above, so as to render the polyurethane charged, wherein the second alcohol in the course of the process is introduced for reaction, for example as defined above. Generally, when using a third alcohol of the type (b) or (c), which requires one or more additional reaction steps in order to introduce a charged group or atom, it is generally preferred to prepare the polyurethane by first reacting the isocyanate groups of the polyisocyanate with the hydroxyl groups of the first, second and third alcohol, and then conducting any additional step(s), e.g. reacting the product obtained with a compound containing an uncharged group or atom capable of charge formation and converting an uncharged group or atom into a charged group or atom. However, such additional step(s) may also be carried out earlier in the process, for example before introducing the last alcohol into the process.

In the process of this invention, the alcohol termed "first alcohol" is a diol, or dihydric alcohol, containing at least 10 carbon atoms. The first alcohol can be selected from aliphatic and aromatic diols, preferably aliphatic diols. The term "aliphatic", as used herein, refers to an essentially hydrocarbon structure apart from designated functional groups, which hydrocarbon structure may be interrupted by one or more heteroatoms, e.g. oxygen

and nitrogen, and/or one or more groups containing heteroatoms, e.g. carbonyl and acyloxy groups. The term "aromatic", as used herein, refers to an aromatic, essentially hydrocarbon structure apart from designated functional groups, which hydrocarbon structure may be interrupted by one or more heteroatoms, e.g. oxygen and nitrogen, and/or one or more groups containing heteroatoms, e.g. carbonyl and acyloxy groups. Suitable first alcohols include high molecular weight polymeric diols, e.g. polyester, polyether and polybutadiene diols, and non-polymeric diols, preferably non-polymeric diols. Preferred first alcohols include aliphatic diols having an aliphatic side-chain substituent. Aliphatic diols carrying an aliphatic substituent may contain from 2 to 20 and suitably from 2 to 10 carbon atoms in the chain connecting the two hydroxyl groups, i.e. in the main chain, and preferred aliphatic main chains include alkylenes and dialkyleneamines. The aliphatic substituent may contain from 1 to 30, suitably at least 10 and preferably from 10 to 22 carbon atoms. Preferred first alcohols are thus selected from aliphatic diols having an aliphatic substituent with at least 10 carbon atoms. When the main chain contains a heteroatom which is nitrogen, it is preferred that the nitrogen carries the aliphatic substituent. Examples of suitable first alcohols include fatty acid monoesters of triols such as glycerol, trimethylolpropane and trimethylolpropane, e.g. monostearates, monobehenates, monopalmitates and monooleates of glycerol and trimethylolpropane; oligomeric esterdiols such as diester diols, e.g. those obtained by reacting a dicarboxylic acid, e.g. adipic acid, with a molar excess of a diol, e.g. ethylene glycols; N-alkyl-diethanolamines, e.g. N-stearyl-diethanolamine; branched chain dihydroxy alkylenes, e.g. 1,2- and 1,4-dihydroxyoctadecanes; and N,N-bis(hydroxyalkyl)-alkylamides, e.g. N,N-bis( $\beta$ -hydroxyethyl)stearylamine. Glycerol monostearate is particularly preferred. Examples of aromatic diols that can be used include bisphenol A. Mixtures comprising two or more first alcohols can also be used.

In the process of this invention, the alcohol termed "second alcohol" can be a low molecular weight diol, or dihydric alcohol, having not more than 8 carbons. The diol can be selected from alkylene diols, e.g. ethylene glycol, propylene glycol, 1,4-butanediol and 1,6-hexanediol; alkyleneoxy diols, e.g. diethylene glycol, triethylene glycol, tetraethylene glycol and dipropylene glycol; and mixtures thereof. Preferred diols include ethylene glycol and diethylene glycol. The diols suitably contain from 2 to 6 carbon atoms and preferably from 2 to 4 carbon atoms. Alternatively, or additionally, the alcohol termed "second alcohol" can be a polyol, or polyhydric alcohol, i.e. an alcohol with at least three hydroxyl groups. Preferably the polyol is aliphatic. Usually the polyol contains from 3 to 10 carbon atoms, notably not more than 8 carbons. Suitable polyols include glycerol, diglycerol, trimethylol ethane, trimethylol propane, and pentaerythritol. Preferred polyols include glycerol, trimethylol propane and pentaerythritol. Among the polyols, it is generally

preferred to use triols and tetraols, preferably triols. The second alcohol should suitably  
b free from charged groups and atoms and also free from groups and atoms capable of  
charge formation.

In the process of this invention, the alcohol termed "third alcohol" is a diol, or  
5 dihydric alcohol, which is charged or capable of charge formation, or a polyol, or  
polyhydric alcohol, capable of further reaction and, optionally, subsequent charge  
formation. Mixtures of third alcohols can also be used. Preferably the third alcohol is an  
aliphatic compound. It is further generally preferred that the third alcohol is a diol. In a  
preferred embodiment of the invention, the process leads to the formation of a  
10 polyurethane which is anionic in nature. In another preferred embodiment of the  
invention, the process leads to the formation of a polyurethane which is cationic in  
nature. In yet another preferred embodiment of the invention, the process leads to the  
formation of an amphoteric polyurethane which, in turn, may be anionic or cationic in  
nature.

15 Accordingly, the third alcohol can be selected from (a) a diol containing a  
charged group or atom, i.e. an anionic or cationic group or atom. In the process, after  
reaction with the polyisocyanate or a preliminary adduct having isocyanate group(s), this  
type of diol produces a charged prepolymer or polyurethane. Examples of anionic groups  
or atoms that can be present in the diol include carboxylate, phosphate and sulfonate  
20 groups, preferably carboxylates, which can be obtained by neutralizing a diol having a  
carboxylic acid or sulfonic acid group, such as the monoester reaction products of triols  
(usually trimethylolethane, trimethylolpropane, glycerol) and dicarboxylic acids or  
anhydrides thereof (usually succinic acid or anhydride, terephthalic acid or anhydride )  
like glycerol monosuccinate, glycerol monoterephthalate, trimethylolpropane mono-  
25 succinate, trimethylolpropane monoterephthalate, N,N-bis-(hydroxyethyl)-glycine, di-  
(hydroxymethyl)propionic acid, N,N-bis-(hydroxyethyl)-2-aminoethanesulfonic acid, and  
the like, by reaction with a base, such as an alkali metal hydroxide, e.g. sodium  
hydroxide, or an amine, e.g. triethylamine, thereby forming an alkali metal or ammonium  
counter-ion. Examples of cationic groups or atoms that can be present in the diol includ  
30 cationically charged sulfur, phosphorous and nitrogen, e.g. in the form of sulfonium  
groups, phosphonium groups and ammonium groups like acid addition salts of primary,  
secondary and tertiary amino groups and quaternary ammonium groups, preferably  
ammonium groups and most preferably acid addition salts of tertiary amino groups and  
quaternary ammonium groups. Examples of suitable cationic diols (a) include acid  
35 addition salts and quaternization products of N-alkandiol dialkylamines and N-alkyl dialka-  
nolamines like 1,2-propanediol-3-dimethylamine, N-methyl diethanolamin , N-ethyl di-

ethanolamin , N-propyl diethanolamine, N-n-butyl diethanolamine and N-t-butyl diethanolamine, N-stearyl diethanolamin and N-methyl dipropanolamine, preferably N-alkyl diethanolamines in which th alkyl groups contain 1 to 4 carbon atoms, in particular N-methyl diethanolamine. The acid addition salts can be derived from acids, such as formic acid, hydrochloric acid, sulfuric acid, etc., and the quaternization products can be derived from alkylating agents like methyl chloride, dialkyl sulfates, e.g. dimethyl sulfate, benzyl halides, e.g. benzyl chloride, epihalohydrins, e.g. epichlorohydrin, and alkylene oxides, e.g. ethylene oxide and propylene oxide. Examples of suitable diols containing a cationic group are disclosed in Internat. Pat. Appl. Publ. No. WO 97/45395 and US Pat. No. 5,561,187, the teachings of which are hereby incorporated herein by reference.

Alternatively, or additionally, the third alcohol can be selected from (b) a diol containing an uncharged group or atom capable of charge formation. In the process, after reaction with the polyisocyanate or a preliminary adduct having isocyanate group(s), this type of diol produces an uncharged prepolymer or polyurethane which is then further reacted in order to produce a charged polyurethane by partially or wholly converting the uncharged groups or atoms derived from the diol (b) into charged groups or atoms. The third alcohol of (b) can be a diol containing a group or atom that can be rendered anionic by reaction with a base. Examples of suitable uncharged groups or atoms of this type include acid groups like sulfonic acid, phosphoric acid and carboxylic acid groups, usually a carboxylic acid group. The anionic charge can be formed by neutralizing the acid group present in the polyurethane by reaction with a base, such as alkali metal hydroxide, e.g. sodium hydroxide, or an amine, e.g. triethylamine, thereby forming an alkali metal or ammonium counter-ion. Suitable non-ionic diols (b) that are potentially anionic include the monoester reaction products of triols (usually trimethylolethane, trimethylolpropane, glycerol) and dicarboxylic acids or anhydrides thereof (usually succinic acid or anhydride, terephthalic acid or anhydride) like glycerol monosuccinate, glycerol monoterephthalate, trimethylolpropane monosuccinate and trimethylolpropane monoterephthalate, as well as N,N-bis-(hydroxyethyl)-glycine, di-(hydroxymethyl)-propionic acid, N,N-bis-(hydroxyethyl)-2-aminoethanesulfonic acid, and the like. Alternatively, the second alcohol of (b) can be a diol containing a group or atom which can be rendered cationic by reaction with an acid or an alkylating agent. Examples of suitable uncharged groups or atoms of this type include sulfur and nitrogen atoms, e.g. in the form of sulfide and amine groups, preferably a nitrogen atom, where the nitrogen can be present as a primary, secondary or tertiary amino group, preferably a tertiary amin group. The cationic charge can be formed by reacting the uncharged groups or atoms present in the polyurethane with an acid and/or alkylating agent, thereby forming cati nic groups or atoms, such as sulfonium and



ammonium groups, e.g. in the form of acid addition salts (protonated nitrogens) and quaternary ammonium groups (quaternized nitrogens). Examples of suitable non-ionic diols (b) that are potentially cationic include N-alkandiol dialkylamines and N-alkyl dialkylamines like 1,2-propanediol-3-dimethylamine, N-methyl diethanolamine, N-ethyl diethanolamine, N-propyl diethanolamine, N-n- and N-t-butyl diethanolamines, N-stearyl diethanolamine and N-methyl dipropanolamine, preferably N-alkyl diethanolamines in which the alkyl groups contain 1 to 4 carbon atoms, in particular N-methyl diethanolamine. Suitable acids include formic acid, hydrochloric acid, sulfuric acid, and the like. Suitable alkylating agents include methyl chloride, dialkyl sulfates, e.g. dimethyl sulfate, benzyl halides, e.g. benzyl chloride, epihalohydrins, e.g. epichlorohydrin, and alkylene oxides, e.g. ethylene oxide and propylene oxide.

The third alcohol can also be selected from (c) a polyol. If this type of third alcohol is used, it is generally preferred that the first and second alcohols have already been introduced into the process and thereby formed a preliminary adduct having terminal isocyanate group(s) in order that the polyol (c) can function as a chain-extend r by reaction with the preliminary adduct to form a polyurethane as well as a reactant for further reaction with a compound (d) which is reactive to hydroxyl groups and contains or introduces a charged group or atom, or an uncharged group or atom capable of charge formation. In the process, when the polyol (c) has been incorporated into the polyurethane by reaction with a preliminary adduct having isocyanate group(s), at least one remaining hydroxyl group derived from the polyol is reacted with the compound (d) and, optionally, any uncharged groups or atoms capable of charge formation derived from the compound (d) are then at least partially converted into charged groups or atoms. Usually the polyol (c) contains from 3 to 10 carbon atoms, notably not more than 8 carbons. Suitable polyols (c) include glycerol, diglycerol, trimethylol ethane, trimethylol propane, and pentaerythritol. Preferred polyols include glycerol, trimethylol propane and pentaerythritol. Among the polyols, it is preferred to use triols and tetraols, preferably triols. Suitable compounds (d) include dicarboxylic acids, dicarboxylic anhydrides and dicarboxylic acid chlorides, preferably dicarboxylic acids and anhydrides, most preferably anhydrides. Suitable dicarboxylic acids, anhydrides and acid chlorides can be selected from aliphatic and/or aromatic compounds containing at least 2 carbon atoms, preferably from 4 to 10 carbon atoms, e.g. succinic acid and anhydride, glutaric acid and anhydride, maleic acid and anhydride, as well as phthalic acid and anhydride. When using a dicarboxylic acid or anhydride, the reaction with a hydroxyl group of the polyol (c) leads to formation of a carboxyl group which can be converted into the corresponding carboxylate group by reaction with a base, such as an alkali metal hydroxide, e.g. sodium

hydroxide, or an amine, e.g. triethylamine. Accordingly, the use of the third alcohol (c) and the compound (d) usually produce anionic groups which may be present in anionic and amphoteric polyurethanes.

If the third alcohol is a polyol (c), it is generally preferred that the second alcohol is selected from diols. However, if the third alcohol is a polyol (c) and the second alcohol is also a polyol, it is preferred that they are different polyols. Polyisocyanates that can be used in the process of this invention include aliphatic, aromatic and mixed aliphatic/aromatic compounds. The term "polyisocyanate", as used herein, refers to a compound with at least two isocyanate groups. Among the polyisocyanates, it is generally preferred to use diisocyanates. Where polyisocyanates containing more than two isocyanate groups are used, e.g. triisocyanates, it is preferred to admix them with diisocyanates. Polyisocyanates generally are known in the art, for example as disclosed in Encyclopedia of Polymer Science and Engineering, Vol. 13, Second Ed., 1988, pp. 243-303, which is hereby incorporated herein by reference. Examples of suitable diisocyanates include toluene-2,4- and 2,6-diisocyanates, diphenylmethane-4,4'-diisocyanate, hexamethylene diisocyanate, dicyclohexylmethane-4,4'-diisocyanate, cyclohexane-1,4-diisocyanate, isophorone diisocyanate and the like. It is also possible to use blocked isocyanates in known manner.

In the present process, the molar ratio of hydroxyl groups of the first, second and third alcohols to isocyanate groups of the polyisocyanate can vary within wide limits depending on, for example, type of alcohols used, type of polyisocyanate used, etc. Usually, the molar ratio of hydroxyl groups to isocyanate groups is within the range of from 0.5:1 to 2:1, suitably from 0.7:1 to 1.3:1 and preferably about 0.9:1 to 1.1:1.

Generally the proportions between the first, second and third alcohols used according to the invention can vary within wide limits. The process is usually carried out using from about 1 to about 80 mole% of (I) hydroxyl groups of the first alcohol, from about 1 to about 75 mole% of (II) hydroxyl groups of the second alcohol and from about 20 to about 90 mole% of (III) hydroxyl groups of the third alcohol, the sum of percentages of (I) + (II) + (III) being 100; suitably (I) is from 5 to 70 mole%, (II) is from 2 to 65 mole% and (III) is from 25 to 70 mole%; and preferably (I) is from 10 to 60 mole%, (II) is from 3 to 50 mole% and (III) is from 25 to 60 mole%. In a preferred embodiment, the first alcohol is used in a predominant amount such that the molar ratios of (I) hydroxyl groups of the first alcohol to (II) hydroxyl groups of the second alcohol and to (III) hydroxyl groups of the third alcohol are both greater than 1:1. Usually these products give improved sizing efficiency.

The process of this invention can be carried out in conventional manner, for example as disclosed in U.S. Pat. Nos. 3,971,764, 4,096,127, 4,617,341, 4,777,224 and

5,561,187, and Internat. Pat. Appl. Publ. No. WO 97/45395, the teachings of which are incorporated herein by reference, except that different reactants are used in this process. As isocyanates are susceptible to nucleophilic attack and readily react with water, the process is preferably carried out in a reaction medium free from water and undesired nucleophiles.

5 Suitably the reaction is carried out in a water-free inert organic solvent, e.g. acetone, optionally in the presence of a catalyst, e.g. diacetoxy-dibutyl-tin. After completed reaction, any further reaction can be carried out and the reaction medium can be worked-up in conventional manner. Examples of useful steps include addition of water, acid, and/or alkali; evaporation of solvent, and the like. Acid and alkali are often added for formation of

10 charged groups in the polyurethane. The polyurethane obtained should suitably be water-soluble or water-dispersable, and water can thus be added for formation of an aqueous polyurethane dispersion. Usually the polyurethane produced has an average molecular weight of at least 500, suitably at least 1,000.

The present invention further relates to the aqueous dispersion of charged

15 polyurethane and the use thereof as an additive in the manufacture of paper. The dispersions may contain from about 1 to 50% by weight of polyurethane, suitably from 5 to 25% by weight. The dispersion may of course be diluted with water prior to use. The term "paper", as used herein, refers to all types of cellulosic products, including paper, board and paper board.

20 In a preferred embodiment, the polyurethane dispersion is used as a sizing agent. The dispersion can be added to the paper making stock (internal sizing agent) or applied to the paper surface (external sizing agent), preferably to surface size paper. In addition to the charged polyurethane, the aqueous composition used for surface sizing, commonly referred to as sizing liquor, usually contains starch or a derivative thereof.

25 Pigments may be present in certain applications. The amount of polyurethane added to the stock or applied to the paper surface may be from 0.001 to 25% by weight, calculated as dry charged polyurethane on dry cellulosic material and optional filler, suitably from 0.01 to 5% by weight. In another preferred embodiment, the dispersion is used as a component of a coating or precoating composition, usually for coating paper. The present coating composition may contain any of the pigments conventionally used in coating and pre-coating

30 compositions including, for example, kaolin, titanium dioxide, calcium carbonate, chalk, aluminum oxide, aluminium silicate, satin white, barium sulfate, silica, talk, calcium sulfate, zink oxide, zirkonium carbonate, magnesium carbonate, the contents of which are usually at least 20% by weight, based on the coating composition. The amount of dispersion of

35 charged polyurethane present in the coating composition can be from 0.01 to 25% by weight, suitably from 0.01 to 8% by weight, calculated as dry polyurethane on dry coating

composition. The amount of coating composition comprising charged polyurethane applied to the paper surface may be within the ranges described above, calculated as dry charged polyurethane on dry cellulosic material and optional filler.

The present invention further relates to a process for surface-treating a material in sheet or web form, e.g. paper or polymeric film, by applying to the surface of the material a composition, e.g. an aqueous composition, comprising the charged polyurethane described herein, and optionally drying the surface-treated material thus obtained. The composition, which can be a surface sizing composition, a pigment coating composition, etc., is suitably applied to the surface in amounts described above, calculated as dry polyurethane on dry material in sheet or web form.

The invention is further illustrated in the following non-limiting examples. Parts and percentages relate to parts by weight and percent by weight, respectively, unless otherwise stated.

#### Example 1

A charged polyurethane according to the invention was prepared as follows: 60.0 ml (420 mmol) of toluene diisocyanate (hereinafter TDI) were added to a solution of 73.1 g (204 mmol) of glycerol monostearate (hereinafter GMS) in 200 g of acetone. The mixture was heated under reflux for 1 h in the presence of a catalytic amount of dibutyl-tin-diacetate. Next, 3.76 g (40.8 mmol) of glycerol were added and heating continued. 35 min later, 17.3 g (129 mmol) of di-(hydroxymethyl)-propionic acid (hereinafter DMPA) and 1.70 g (14.3 mmol) of N-methyl-diethanolamine (hereinafter N-MDEA) in 200 g acetone were added. The reaction mixture was heated under reflux for additional 1 h and then treated with 116 ml of 1 M NaOH (aq) and 1000 ml water. The acetone was evaporated in vacuum yielding an aqueous dispersion of anionic polyurethane.

#### Example 2

A charged polyurethane according to the invention was prepared essentially as in Example 1 except that TDI was added to an acetonic solution of both GMS and glycerol. After heating under reflux for 70 min, DMPA and N-MDEA were added as above followed by heating the reaction mixture under reflux for additional 2 h. The reaction mixture was worked-up as in Example 1, yielding an aqueous dispersion of anionic polyurethane.

#### Example 3

A charged polyurethane according to the invention was prepared essentially as in Example 1 except that 5.0 g (54.3 mmol) of glycerol, 14.8 g (110 mmol) of DMPA, 1.46 g (12.3 mmol) of N-MDEA and 100 ml of 1 M NaOH were used. Working-up the reaction mixture yielded an aqueous dispersion of anionic polyurethane.

Example 4

A charged polyurethane according to the invention was prepared essentially as in Example 1 except that glycerol was replaced with 3.8 g (61.2 mmol) of ethyleneglycol. Working-up the reaction mixture yielded an aqueous dispersion of anionic polyurethane.

5

Example 5

A charged polyurethane according to the invention was prepared essentially as in Example 1 except that glycerol was replaced with 5.5 g (61.2 mmol) of 1,4-butanediol. Working-up the reaction mixture yielded an aqueous dispersion of anionic polyurethane.

Example 6

10

A charged polyurethane according to the invention was prepared essentially as in Example 1 except that glycerol was replaced with 7.2 g (61.2 mmol) of 1,6-hexanediol. Working-up the reaction mixture yielded an aqueous dispersion of anionic polyurethane.

Example 7

15 A charged polyurethane according to the invention was prepared essentially as in Example 1 except that glycerol was replaced with 4.7 g (61.2 mmol) of 1,2-propanediol. Working-up the reaction mixture yielded an aqueous dispersion of anionic polyurethane.

Example 8

20 A charged polyurethane according to the invention was prepared essentially as in Example 1 except that glycerol was replaced with 4.2 g (30.6 mmol) of pentaerythritol. Working-up the reaction mixture yielded an aqueous dispersion of anionic polyurethane.

Example 9

25 For comparison purposes, a charged polyurethane was prepared following the procedure according to Example 1 except that no glycerol was used and the amounts of DMPA, N-MDEA and 1 M NaOH were 24.6 g (183 mmol), 2.43 g (20.4 mmol) and 165 ml, respectively. Working-up the reaction mixture yielded an aqueous dispersion of anionic polyurethane.

Example 10

30 For comparison purposes, a charged polyurethane was prepared according to the teachings of U.S. 4,777,224, as follows: 15 ml (105 mmol) of TDI were added to a solution of 18.3 g (51.0 mmol) of GMS in 50 g of acetone. The mixture was heated under reflux for 1 h in the presence of a catalytic amount of dibutyl-tin-diacetate. Next, 2.85 g (21.2 mmol) of DMPA, 2.58 g (21.7 mmol) of N-MDEA in 50 g acetone and 13.8 g (6.89 mmol) of polyethylene glycol with an average molecular weight of 2000 were added. The reaction mixture was heated under reflux for additional 90 min and then treated with 14.4 ml of 1 M NaOH (aq) and 250 ml water. The acetone was evaporated in vacuum yielding  
35 an aqueous dispersion of anionic polyurethane.

Example 11

A charged polyurethane according to the invention was prepared as follows: 15 ml (105 mmol) of TDI were added to a solution of 18.3 g (51.0 mmol) of GMS in 50 g of acetone. The mixture was heated under reflux for 1 h in the presence of a catalytic amount of dibutyl-tin-diacetate. Next, 0.94 g (10.2 mmol) of glycerol were added and heating continued. 25 min later, 1.97 g (7.65 mmol) of N-MDEA quaternized with epichlorohydrin (a hydroxy-functional quaternary ammonium compound prepared according to the teachings of WO 97/45395; hereinafter N-MDEA-ECH) and subsequently 3.34 g (28.1 mmol) of N-MDEA in 50 g acetone were added. The temperature was increased and the reaction mixture was heated under reflux for 50 min. The resulting acetic solution was poured into 27 ml of 1 M HCl (aq) and 250 ml water. Acetone was removed in vacuum giving an aqueous dispersion of cationic polyurethane.

Example 12

A charged polyurethane according to the invention was prepared essentially as in Example 11 except that no N-MDEA-ECH was used and the amounts of N-MDEA and 1 M HCl were increased to 4.26 g (35.7 mmol) and 34 ml, respectively. The product obtained was an aqueous dispersion of cationic polyurethane.

Example 13

For comparison purposes, a charged polyurethane was prepared following the procedure according to Example 11 except that no glycerol was used and the amounts of N-MDEA and 1 M HCl were increased to 5.17 g (43.4 mmol) and 39 ml, respectively. The product obtained was an aqueous dispersion of cationic polyurethane.

Example 14

For comparison purposes, a charged polyurethane was prepared following the procedure according to Example 12 except that no glycerol and no N-MDEA-ECH were used and the amounts of N-MDEA and 1 M HCl (aq) were increased to 6.08 g (51.0 mmol) and 48.5 ml, respectively. The product obtained was an aqueous dispersion of cationic polyurethane.

Example 15

Sizing efficiency of the anionic polyurethane dispersions according to Examples 1-10 was evaluated by means of the Cobb test, using German DIN standard 5312 which is a common method in the art. The Cobb<sub>60</sub> values correspond to paper absorption of water, expressed in g/m<sup>2</sup> of water take-up after 1 min contact time.

Sizing liquor containing the polyurethane dispersion was applied with a laboratory size press to an unsized base paper. The sizing liquor also contained 5% of oxidatively degraded starch.

13

The values measured on the sized paper sheets are presented in Table 1, where dosage of the polyurethane dispersion (in %) refers to dry anionic polyurethane on dry paper.

Table 1

Polyurethane Dispersion used	Cobb <sub>60</sub>			
	0.075 %	0.10 %	0.15 %	0.2 %
Example No. 1	-	24	22	21
Example No. 2	40	28	25	23
Example No. 3	-	26	22	21
Example No. 4	-	35	23	21
Example No. 5	-	33	23	22
Example No. 6	-	36	24	21
Example No. 7	-	62	26	23
Example No. 8	-	24	22	20
Example No. 9 (comparison)	88	75	34	28
Example No. 10 (comparison)	-	85	31	25

5

As can be seen from Table 1, the sizing efficiency of the polyurethane dispersions of Examples 1 to 8 according to the invention showed significant improved sizing efficiency over polyurethane dispersion of Examples 9 and 10 used for comparison.

10

Example 16

Sizing efficiency of the cationic polyurethane dispersions according to Examples 11-14 was evaluated as in Example 15. The results are presented in Table 2, where dosage of the polyurethane dispersion (in %) refers to dry cationic polyurethane on dry paper.

15

Table 2

Polyurethane Dispersion used	Cobb <sub>60</sub>	
	0.10 %	0.15 %
Example No. 11	61	25
Example No. 12	79	27
Example No. 13 (comparison)	82	33
Example No. 14 (comparison)	88	45

14

As can be seen from Table 2, the sizing efficiency of the polyurethane dispersion of Examples 11 and 12 according to the invention showed significant improved sizing efficiency over polyurethane dispersion of Examples 13 and 14 used for comparison.

5



Claims

1. A process for the production of charged polyurethanes comprising reacting isocyanate groups of a polyisocyanate with hydroxyl groups of different alcohols comprising  
(i) a first alcohol selected from one or more diols containing at least 10 carbon atoms;  
5 (ii) a second alcohol selected from alkylene diols having not more than 8 carbon atoms, alkyleneoxy diols having not more than 8 carbon atoms, polyols, and mixtures thereof;  
(iii) a third alcohol selected from (a) diols containing a charged group or atom, (b) diols containing an uncharged group or atom capable of charge formation and at least partially converting the uncharged group or atom into a charged group or atom, (c) polyols and  
10 further reaction of one or more hydroxyl group derived from the polyol with a compound containing a charged group or atom or a compound containing an uncharged group or atom capable of charge formation and at least partially converting said uncharged group or atom into a charged group or atom, and mixtures thereof.

2. A process for the production of charged polyurethanes according to claim 1,  
15 c h a r a c t e r i s e d in that in the production of anionic polyurethanes, the first alcohol is an aliphatic diol having an aliphatic side-chain substituent having at least 10 carbon atoms.

3. A process for the production of charged polyurethanes according to claim 1 or 2, c h a r a c t e r i s e d in that the polyurethane is anionic.

20 4. A process for the production of charged polyurethanes according to claim 1, c h a r a c t e r i s e d in that the polyurethane is cationic.

5. A process for the production of charged polyurethanes according to claim 1, c h a r a c t e r i s e d in that the polyurethane is amphoteric.

6. A process according to any of the preceding claims, c h a r a c t e r i s e d in  
25 that the third alcohol is selected from (a) diols containing a charged group or atom, (b) diols containing an uncharged group or atom capable of charge formation, and mixtures thereof.

7. A process according to any of the preceding claims, c h a r a c t e r i s e d in that the first and second alcohols are introduced into the process for reaction before  
30 introducing the third alcohol.

8. A process according to any of the preceding claims, c h a r a c t e r i s e d in that (i) the first alcohol is an aliphatic diol having an aliphatic substituent with at least 10 carbon atoms; (ii) the second alcohol is selected from diols, triols, tetraols, and mixtures thereof; and (ii) the third alcohol is selected from N-alkandiol dialkylamines, acid addition  
35 salts thereof and quaternization products thereof, N-alkyl dialkanolamin s, acid addition salts thereof and quaternization products thereof, diols containing a carboxylic acid

group, diols containing a carboxylate group, diols containing a sulfonic acid group, diols containing a sulfonat group, and mixtures thereof.

9. A process according to any of the preceding claims, c h a r a c t e r i s e d in that the process is carried out using from 10 to 60 mole% of (I) hydroxyl groups of the first alcohol, from 3 to 50 mole% of (II) hydroxyl groups of the second alcohol and from 25 to 60 mole% of (III) hydroxyl groups of the third alcohol, the sum of percentages of (I) + (II) + (III) being 100.

10. Charged polyurethane obtainable by a process according to any one of claims 1 to 9.

10 11. Aqueous dispersion containing a charged polyurethane according to claim 10 or containing a charged polyurethane produced according to any of claims 1 to 9.

12. A method of surface-treating a material in sheet or web form by applying a composition to the surface of the material, c h a r a c t e r i s e d in that the composition comprises a charged polyurethane according to claim 10 or an aqueous dispersion  
15 containing a charged polyurethane according to claim 11.

13. A method according to claim 12, c h a r a c t e r i s e d in that the material in sheet or web form is a cellulosic product.

14. A method according to claim 12 or 13, c h a r a c t e r i s e d in that it is a surface sizing method which is carried out using an aqueous sizing composition.

20 15. A method according to claim 12 or 13, c h a r a c t e r i s e d in that it is a paper coating method which is carried out using an aqueous pigmented composition.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/SE 99/01113

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08G18/08 C08G18/66 C08G18/80 D21H17/57

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08G D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 268 806 A (AKZO NV) 1 June 1988 (1988-06-01) page 3, line 6 -page 3, line 36 example 3 claim 2 & US 4 777 224 A ---	1-15
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Y	US 4 096 127 A (SCHURMANN HORST ET AL) 20 June 1978 (1978-06-20) cited in the application claim 2; example 6 ---	1-15
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents:

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# INTERNATIONAL SEARCH REPORT

International Application No

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